Indian J. Phys. 71A (4), 409–420 (1997)

IJP A
- an international journal

Electron structure and configurational energy of hydrogen in magnesium using nonlinear response theory

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Received 7 October 1996, accepted 9 December 1996

Abstract : Induced charge density, configurational energy, residual resistivity are calculated using nonlinear response theory following the procedure of Manninen and Nieminen The lattice contribution is included through spherical solid model potential (SSMP) The effect of SSMP is found to be significant (10%) in all the properties of interest The calculated configurational energy predicts that hydrogen prefers octahedral (O)-sites in Mg matrix. A shallow s-type bound state energy of electron -0.776×10^{-8} ryd. suggests that magnesium does not form Mg–H compound and hydrogen stays as a free ion in the magnesium.

Keywords : Spherical solid model potential, electron structure and configurational energy, nonlinear response theory

PACS No. : 66.30.Jt

1. Introduction

Until the late sixties, research on electronic properties of metal hydrides involved mainly experimental work [1]. The first theoretical investigations started in early fifties with the pioneering work of Friedel [2] in which he studied the screening of a hydrogen impurity and heat of solution of H in noble metals. The first *ab initio* bandstructure calculations on binary hydrides performed by Swetendick [3] gave a new impetus and stimulated a lot of experimental and theorical work. From theoretical results on concentrated hydrides, several important features have emerged and the hydrides are no longer considered, as they were in early days, as interstitial alloys but rather a real compounds.

A substantial number of theoretical studies of a hydrogen impurity in simple metals have appeared since mid 70's; most of them are based on jellium model [4–7]. The effect of lattice ions is introduced using approximate treatments, such as, the spherical solid model potential [8–11]. Other theoretical treatments of H in simple metals using

supercell model [12], KKR Green function method [13] have also been used. The later two methods, which are better than jellium model, have not become popular because they require heavy computational efforts. Studies of heat of solution of H, determination of hydrogen site occupancies, activation energies for overcoming potential barrier as involved in classical diffusion mechanism and calculations of local mode vibration frequencies are available. Attempts to study lattice relaxation effects around the H impurity in simple metals have also been made. The corresponding theoretical work on simple metals has been recently reviewed [14].

Magnesium forms transparent insulating saline hydrides [1]. Though this light weight hydride is of potential interest for hydrogen storage, very little is known about its electronic properties [15]. Therefore, we thought it worthwhile to study the electronic structure, configurational energy, activation energy, self-energy, charge transfer and residual resistivity of H in Mg following the procedure of Manninen and Nieminen [8] where the host-ion contribution is added in the effective potential of hydrogen through spherical solid model potential (SSPM). Even though linear-response theory is inadequate for describing the screening of a proton in a metal, it is convenient to develop first of all, the linear pseudopotential theory of induced charge density and configurational energy. Therefore, electron charge density and activation energy of hydrogen using linear-response theory are also calculated and compared with the results of nonlinear response theory.

The plan of the paper is as follows : The necessary formalism is presented in Sections 2 and 3. The calculations and results are presented in Section 4. The results are summarized in Section 5.

2. Linear response theory

The induced charge density $\delta n_i(r)$ and its Fourier transform $\delta n_i(q)$ are related through the following expression :

$$\delta n_i(r) = \frac{1}{(2\pi)^3} \int dq\, \delta n_i(q) e^{iq.r},$$

where $\delta n_i(q)$ in linear screening theory is given by

$$\delta n_i(q) = -\frac{q^2}{4\pi}\left(1 - \frac{1}{\varepsilon(q)}\right)\delta V_i(q), \tag{2}$$

In eq. (2), $\delta V_i(q)$ is the Fourier transform of the impurity potential $\delta V_i(r)$. $\varepsilon(q)$ is the Lindhard dielectric function modified for exchange correlation corrections due to Taylor [16]. For spherical symmetric potential $\delta V_i(r)$, eq. (1) simplifies to

$$\delta n_i(r) = -\frac{1}{8\pi^3}\int_0^\infty dq\, q^4 \frac{\sin(qr)}{qr}\left(1 - \frac{1}{\varepsilon(q)}\right)\delta V_i(q), \tag{3}$$

in linear screening approximation.

3. Nonlilinear response theory

3.1 Size effect :

Due to hydrogen absorption at interstial positions, the host ions are generally displaced out except in some special cases where lattice contraction takes place. Therefore, the positive charge density decreases and electronic charge density increases in the vicinity of the impurity. As a result the positive charge on the impurity changes. The net charge on the proton is given by [17]

$$Z_{\text{eff}} = Z_p - \frac{\delta V}{V} Z_H, \tag{4}$$

where Z_p and Z_H are ionicity of the proton and host ion, respectively. $\delta V/V$ is the fractional charge in the atomic volume of host ion. In the continuum model of lattice, $(\delta V/V)$ is taken as local dilation around the impurity and is given as

$$\frac{\delta V}{V} = \left(\frac{3}{\gamma}\right)\left(\frac{1}{a}\frac{da}{dc}\right) \tag{5}$$

where $\gamma = [3(1 - \sigma)/(1 + \sigma)]$, σ is Poisson ratio, $(da/dc)/a$ is the ralative change in lattice parameter a in percent per atomic percent impurity and c is the concentration of impurity

3.2 Spherical solid model potential (SSMP) :

For a system of N ions, the total potential is given by the sum of potentials $w(|r - r_l|)$ of the individual atoms situated at the position r_l, *i.e.*,

$$V_H(r) = \sum_l w\left(|r - r_l|\right) \tag{6}$$

The solution of Schrödinger equation becomes cumbersome by taking exact form of $V_H(r)$, therefore, we consider only the spherical part of $V_H(r)$ by taking its angular average as follows [8] :

$$V_{\text{av}}(r) = \frac{1}{4\pi}\int d\Omega \sum_l w_H\left(|r - r_l|\right), \tag{7}$$

where $d\Omega$ is the solid angle. By including the potential due to jellium charge density $n_0 = 3/4\pi r_s^3$, where r_s is electron density parameter, the spherical solid model potential (SSMP) takes the form

$$V_{ss}(r) = \frac{1}{4\pi}\int d\Omega \sum_l w_H\left(|r - r_l|\right) + \int \frac{dr' n_0}{|r - r'|}. \tag{8}$$

3.3 Configurational energy :

The proton-host interaction energy in second-order perturbation theory is given by [18] :

$$\Delta E(R_p) = \sum_l \frac{Z_p Z_H e^2}{|r_p - r_l|} + \int dr\, \delta n(r - r_p) \sum_l w_H(r - r_l), \tag{9}$$

where r_p is the position vector of the proton and R_p represents the relative position of hydrogen with respect to some interstitial site. Taking the Fourier transform of second term in (9) and then solving it, we arrive at the following result :

$$\Delta E(R_p) = \sum_l \frac{Z_p Z_H e^2}{|r_p - r_l|} - \sum_l \frac{Z_p Z_H e^2}{|r_p - r_l|} \int dq\, \delta n(q) w_H(q) \frac{\sin\left(q|r_p - r_l|\right)}{q|r_p - r_l|} \tag{10}$$

where $w_H(q)$ and $\delta n(q)$ are the Fourier transform of $W_H(r)$ and $\delta n(r)$, respectively. Rearranging the various terms in (10), we finally get

$$\Delta E(R_p) = \frac{2Z_p e^2}{\pi} \sum_l \frac{1}{|r_p - r_l|} \left\{ \frac{\pi Z_H}{2} - Z_H \int dq\, \delta n(q) w_H(q) \frac{\sin\left(q|r_p - r_l|\right)}{q} \right\}, \tag{11}$$

where we have chosen the Ashcroft [19] potential with core radius $r_c = 1.39$ a.u. to represent the magnesium ion.

3.4. Induced charge density and impurity potential .

In order to find impurity potential, Popovic *et al* [4] considered the case of a single proton in homogeneous electron gas. Following Popovic *et al* [4], the induced electron charge density is written as

$$\delta n(r) = n(r) - n_0(r) = \frac{1}{\pi^2} \int_0^{k_f} dk k^2 \sum_l (2l+1) \left[R_{lk}^2(r) - j_l^2(kr) \right] + 2R_b^2(r), \tag{12}$$

where k is the electron wave vector, and k_F is the Fermi momentum. $j_l(kr)$ are spherical Bessel functions corresponding to angular momentum quantum number l. s-type bound state sometimes occur; therefore, the bound state charge density $R_b^2(r)$ is also added in (12).

The electron eigen values e_k and corresponding radial function $R_{lk}(r)$ are obtained by solving the following one particle Schrödinger equation :

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r) + \frac{l(l+1)}{2r^2} - \varepsilon_k \right] r R_{lk}(r) = 0. \tag{13}$$

For the continuum states $\varepsilon_k = k^2/2$, zero of energy is taken to be the potential far from the impurity where its effect almost vanishes. The effective potential field, in which the electron moves, is written as

$$V_{\text{eff}}(r) = -\frac{Z}{r} + V(r) + V_{ss}(r) + V_{xc}\left(n(r)\right) - V_{xc}\left(n_0(r)\right), \tag{14}$$

for a spherically symmetric potential field. $V_{xc}(n(r))$ is the functional derivative of a universal exchange and correlation-energy functional $E_{xc}(n(r))$ of particle density $n(r)$. Eqs. (13) and (14) are solved self-consistently. The impurity potential

$$V(r) = \int \frac{\delta n(r')dr'}{|r-r'|} \tag{15}$$

can be obtained by solving Poisson equation

$$\nabla^2 V(r) = -4\pi\delta n(r). \tag{16}$$

Ideally, the potential $V(r)$ and the charge density $\delta n(r)$ should be determined self-consistently so that the eigenstates $R_{lk}(k)$ yield a charge density which is identical to that obtained from (16). In the crystal, the conduction electrons are represented by the Bloch functions. As a result, the impurity site will no longer follow the spherical symmetry of jellium model and the solution of second-order partial differential equation (13) for single electron eigen states becomes very cumbersome. Success has been achieved recently in the self-consistent solution for a proton in jellium by taking the spherical part of the host-ion potential $V_{ss}(r)$, around impurity [8,9,20].

After adding $V_{ss}(r)$ in (14), it is not always possible to find out convergent solution of eq. (13) following the procedure of Popovic *et al* [4]. Therefore, Manninen *et al* [21] suggested that the impurity potential $V(r)$ may be obtained by rewriting the Poisson equation as :

$$\nabla^2 V(r) - k_{TF}^2 V(r) = -4\pi\delta n(r) - k_{TF}^2 V(r). \tag{17}$$

By solving (17), we get

$$V(r) = \frac{1}{4\pi}\int dr \frac{\exp\left(-k_{TF}|r-r'|\right)}{|r-r'|}\left\{4\pi\delta n(r') + k_{TF}^2 V(r')\right\}, \tag{18}$$

k_{TF} is Thomas-Fermi (TF) screening parameter $(4K_F/\pi)^{1/2}$. The TF potential may be chosen as the initial potential for starting the iteration. In the present calculation, the initial potential is taken of the form

$$V_{\text{eff}}^{(0)}(r) = -\frac{Z}{r}\left(1 + \frac{\beta r}{2}\right)\exp(-\beta r), \tag{19}$$

instead of TF potential, because it provides an accurate description of a proton impurity in both electron gas and transition metal [22]. The parameter β is determined self-consistently, so that $V_{\text{eff}}^{(0)}$ may satisfy the Friedel sum rule

$$Z = \frac{2}{\pi}\sum_l (2l+1)\,\delta_l(k_F), \tag{20}$$

with high accuracy. $\delta_l(k_F)$ is the phase shift at Fermi sphere corresponding to angular momentum quantum number l. By solving (13) and (14) numerically, we get a new potential $V_{\text{eff}}^{(1)}(r)$, which can be inserted again into (13) for next iteration. This procedure has to be repeated until the potential $V_{\text{eff}}^{(1)}(r)$ and $V_{\text{eff}}(r)$ satisfy the Friedel sum rule

simultaneously. In this procedure, the Coulombic tail, if persists, gets truncated due to the exponential term. The self-consistency is achieved within 2% in the charge density Eq (13) leads to a convergence after about 10 iterations when starting from $V_{\text{eff}}^{(0)}(r)$.

4. Calculations and results

4.1 Effective charge on the proton :

The effective charge on the proton in Mg metal is estimated using (1). The value of $\delta V/V$ is estimated from the ratio of the moduli of rigidity [17]. This value comes out to be 0.21e The effective charge Z on the proton after taking the size effect comes out to be 0.58e.

4.2 Spherical solid model potential (SSMP) :

The atomic radius r_0 and c/a ratio for Mg are taken to be 3.3514 a.u and 1.623, respectively. The effective charge of the proton and bare host-ion charge are taken 0.58e and 2e, respectively. The summation in eq. (8) is carried out upto 26th shell. The calculated $V_{ss}(r)$ using (8) around octahedral (O) and tetrahedral (T)-sites are shown in Figure 1. The

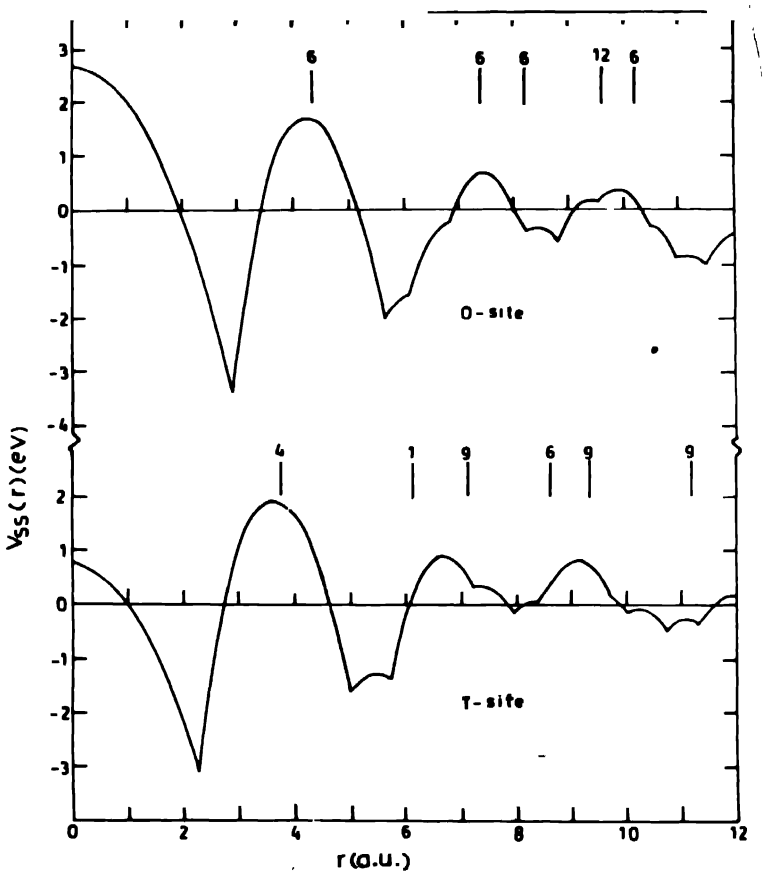

Figure 1. The spherical solid model potential (SSMP) $V_{ss}(r)$ for Mg around octahedral (O)-site and tetrahedral (T) site. The Positions and number of nearest neighbours to octahedral (tetrahedral)-site are also indicated there

number of nearest neighbours and their positions with respect to O(T)-site are also indicated there. From Figure 1, it is clear that Mg is more densely packed around T-site. $V_{ss}(r)$ has the maxima around the near neighbour sites and minima between the two sites. It does not show exact periodicity of the lattice, therefore, it can be regarded just as a correction term to $V_{eff}(r)$ for the discrete nature of the lattice. The relative magnitude of $V_{ss}(r)$ also depends upon Z_H and r_c, because it is shifted upward by a constant amount $3r_c^2 / 2r_s^2$, which is obtained by taking $q \to 0$ limit of first part of $V_{ss}(r)$ in eq. (8).

4.3 Electron structure of hydrogen :

The calculations of induced charge density $\delta n(r)$ is done by solving eqs. (13) and (14) following the procedure of Manninen and Nieminen [8]. The parametrized form of $V_{xc}(n(r))$ proposed by Gunnarson and Lundquist [23] has been taken for detailed calculations. In the first step, the calculation is done for the perfect crystal by putting $n(r) = n_H(r)$, $Z = 0$ and $\delta n(r) = n_H(r) - n_0$. The self-consistently calculated $V_H(r)$ and $\delta n_H(r)$ are obtained.

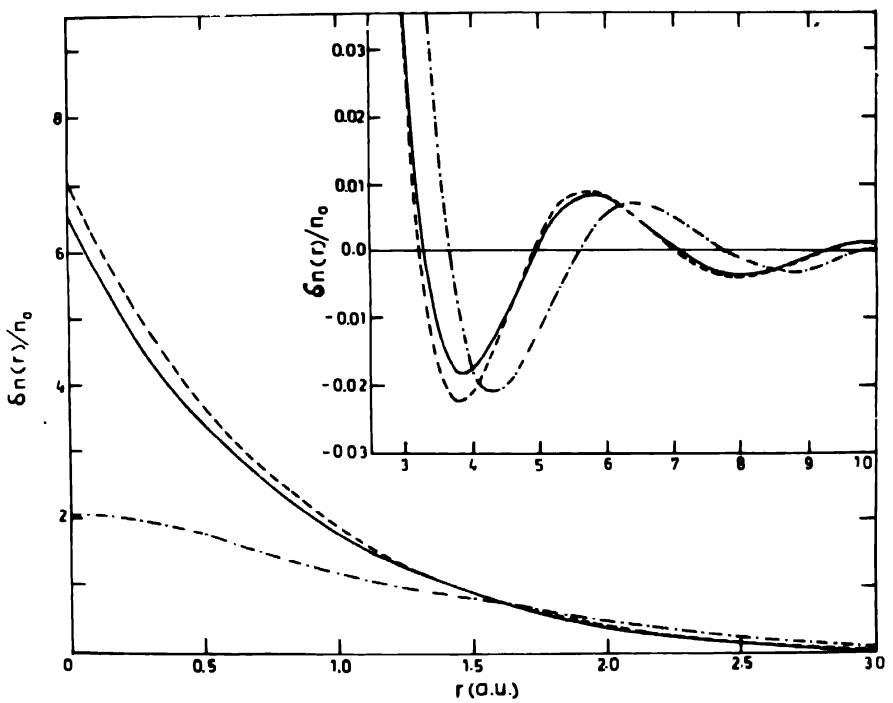

Figure 2. The ratio of proton induced charge density and electron charge density $\delta n_p(r)/n_0$. The solid and dashed lines represent $\delta n(r)/n_0$ obtained by including $V_{ss}(r)$ and without including it, respectively. The dash-dot line represents $\delta n(r)/n_0$ obtained by using linear response theory. The results in the inset are given on a magnified scale.

In the second step, the calculation is repeated with impurity at interstitial site by putting $n(r) = n_p(r)$, $Z = Z_{eff}$, $\delta n(r) = n_p(r) - n_0$ and self-consistently calculated

$V_p(r)$ and $\delta n_p(r)$ are obtained. In both cases, the Friedel sum rule (20) is satisfied. The difference

$$\delta V_i(r) = V_p(r) - V_H(r), \tag{21}$$

and

$$\delta n_i(r) = \delta n_p(r) - \delta n_H(r), \tag{22}$$

give the impurity interaction potential and the impurity induced charge density, respectively.

The impurity induced charge density $\delta n_i(r)$ calculated using (22) in Mg, is shown in Figure 2 by solid and dashed lines with and without inclusion of $V_{ss}(r)$, respectively. There is a pile up of charges on the impurity site. It decreases rapidly with increasing r and becomes oscillatory beyond $r = 4.0$ a.u. The SSMP reduces the induced charge density at $r = 0$ by about 10%. It is found that the linear screening theory grossly underestimates the induced charge density (shown by dash-dot line) by a factor of 2.25 at $r = 0$. This indicates the importance of $V_{ss}(r)$ and nonlinear screening theory while calculating the induced charge density of hydrogen in Mg.

4.4 Self energy of the proton :

The attractive potential of the proton affects those metal wave functions which have a finite density at the H-site and leads to the so called metal hydrogen bonding band below the metal d-band. Further it can pull below the Fermi energy E_F some metal states which were located above E_F in the pure metal. The amount of binding energy by which the attractive effective potential of an impurity brings down the impurity in lower state is called the self-trapped energy or self-energy of an impurity. By solving Poisson equation using the analytical form $V_{\text{eff}}^{(0)}(r)$ given by (19), one can obtain the charge density

$$\delta n_i(r) = \frac{Z\beta^3}{8\pi} \exp(-\beta r). \tag{23}$$

At $r = 0$, eq. (23) reduces to

$$\delta n_i(0) = \frac{Z\beta^3}{8\pi}. \tag{24}$$

By putting the value of $\delta n_i(0)$ in (24), one can get the value of the parameter β. The value of β so obtained is 1.5282 a.u. Substituting the value of $\delta V_i(r) = V_{\text{eff}}^{(0)}(r)$ and $\delta n_i(r)$ from (23), the self-energy

$$E_{sc} = \frac{1}{2}\int \delta v_i(r)\,\delta n(r)\,dr, \tag{25}$$

reduces to

$$E_{sc} = -\frac{3}{32} Z^2\beta \text{ a.u.} \tag{26}$$

The self-energy of proton in Mg is found to be – 0.048 a.u.

We have also calculated the electron charge within the core of hydrogen by integrating $\delta n_i(r)$ from 0 to core radius (1 a.u.). It is found to be 0.13e. This gives the net charge on the proton $n_s = Z - Z_{core} = 0.45e$.

4.5. Configurational energy :

The calculated configuration energy using (11) along O-O (octahedral), O-T (tetrahedral) and T-T directions in the $(11\bar{2}0)$ plane is shown in Figure 3. The configurational energy is found to be maximum exactly at mid-point of both T-T and O-O paths. Along T-O path, it is found to be maximum at about 33% distance of T-O path. Octehedral position is found to be the most favourable position for the hydrogen impurity to stay in, as the configurational

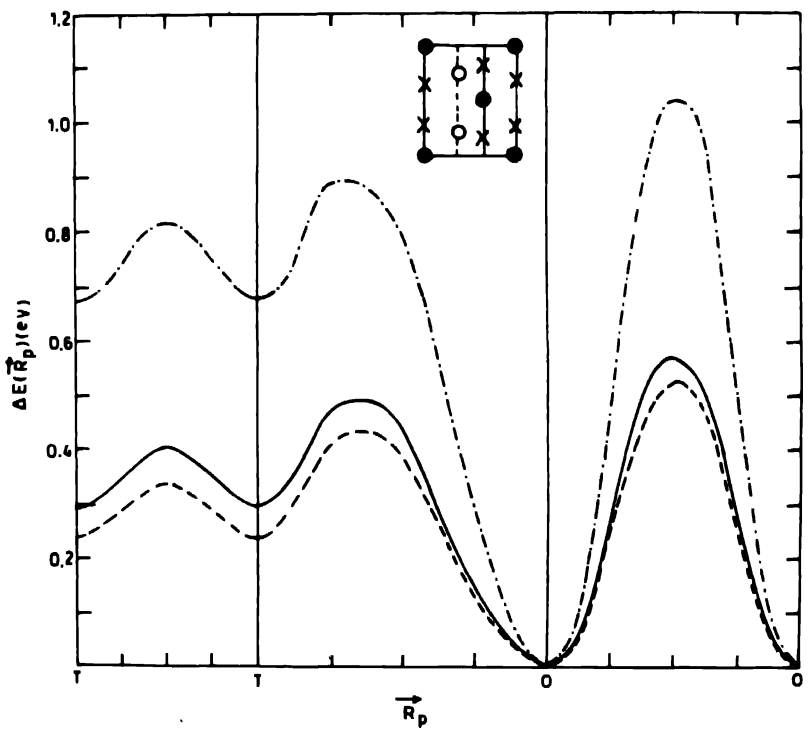

Figure 3. The configurational energy $\Delta E(R_p)$ of protron in Mg. The solid and dashed lines represent $\Delta E(R_p)$ calculated by including and without including $V_{ss}(r)$, respectively The dash-dot line represent the configurational energy obtained using linear response theory Inset O → octahedral positions ; X → tetrahedral positions ; ● → host ions

energy is minimum at O-site. The migration energy along O-O, O-T and T-T paths are found to be 0.57 eV, 0.49 eV and 0.41 eV, respectively. The corresponding values by putting off $V_{ss}(r)$ are found to be 0.53 eV, 0.43 eV and 0.34 eV, respectively. This shows that $V_{ss}(r)$ changes the scattering around the impurity considerably. For Mg, experimentally determined values of migration energy are not available. The linear response theory

overestimates the migration energies for Mg and the results are 1.05 eV, 0.89 eV and 0.82 eV for O-O, O-T and T-T jumps, respectively, Popovic *et al* [4] have also calculated the migration energy of hydrogen in Mg using nonlinear response theory by ignoring lattice contribution and size effect. The values of migration energy obtained by them along O-O and O-T path are 0.34 eV and 0.27 eV, respectively. The corresponding two values calculated presently are 0.53 eV and 0.43 eV. The two calculations agree qualitatively. Our calculated values of migration energy differ in magnitude from the values obtained by Popovic *et al* [4] because of three reasons : (i) Popovic *et al* [4] have used the exchange correlation correction functional suggested by Hedin and Lundquist [24], while in the present calculations, the comparatively recent one, suggested by Gunnarson and Lundquist [23] is used. (ii) We have used a different procedure suggested by Manninen and Nieminen [8] to achieve the convergent solution of Schrödinger equation because the self-consistent procedure followed by Popovic *et al* [4] does not always converge after adding $V_{ss}(r)$ in the $V_{eff}(r)$. (iii) Popovic *et al* [4] have ignored the size effect while doing full calculation of induced charge density and configurational energy, *i.e.*, they have done full calculation of $\delta n(r)$ and $\Delta E(R_p)$ by considering $Z_{eff} = 1.0$.

In the present calculations, no account has been taken of relaxation energies of ions around the proton. The forces acting on the neighbouring ions could be calculated from the displaced electron density and the relaxed positions of the ions using the standard methods of lattice statistics. This would be a lengthy calculation and probably unprofitable in view of the small relaxation energy.

4.6 Phase shifts and residual resistivity :

The phase shifts are obtained while solving the Schrodinger equation using partial phase shift analysis. The s and p phase shifts are found to dominate. By including $V_{ss}(r)$, the s and p phase shifts change by 10%. The residual resistivity $\Delta\rho$ is estimated using the expression for the liquid phase [25] by taking first seven phase shifts for dilute Mg–H system because the values $\delta_l(k_F)$ are found to be too small beyond $l = 6$. Our calculated value of $\Delta\rho$ is found to be 0.62 μΩ cm/at%. The value of $\Delta\rho$ by putting off SSMP ($V_{ss}(r) = 0$) comes out to be 0.67 μΩ cm/at% which is about 10% higher than that obtained by including $V_{ss}(r)$. Thus the lattice contribution is essential to give the correct description of residual resistivity of dilute metal-hydrogen system.

5. Conclusions

The electron structure, migration energy, self-energy, charge transfer and residual resistivity of H in Mg are calculated using nonlinear response theory with and without the inclusion of the lattice contributions. Although $V_{ss}(r)$ is included in an approximate manner, it changes the induced charge density near the impurity, migration energies and residual resistivity by

about 10%. Therefore, the lattice contribution is necessary to take account of proper scattering around proton. Our calculated configurational energy predicts that H prefers octahedral sites in Mg. The linear response theory under-estimate the induced charge density near the impurity by a factor of two, while it over-estimates the migration energies by a factor of two. Therefore, for calculating electron-proton interaction, nonlinear theory is essential. A very shallow s-type bound state of energy (-0.776×10^8 ryd) suggests that there is a weak binding of proton and electron and that hydrogen does not form Mg–H compound. Because of this reason, the light-weight material Mg may become a potential source for hydrogen storage in future.

Acknowledgments

The authors wish to thank Dr. V C Sahni and Dr. R C Srivastava for the encouragement to carry out this work. The authors are also grateful to Prof. S Prakash and Dr. D K Avasthi for stimulating discussions at various stages of this work. The financial support from the Department of Science & Technology, Government of India for this project is gratefully acknowledged.

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